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⑷ A tin coating immersion solution and a coating process using the same.

⑸ The invention provides an immersion coating bath solution for depositing a tin coating on a bimetal bearing having one portion thereof composed of an aluminum base metal and another portion of the surface thereof composed of a ferrous base, the solution having an acidic pH and comprising a water soluble stannous salt and a wetting agent. The invention also provides a process for depositing a tin coating on a bimetal bearing having one portion thereof composed of an aluminum base metal and another portion of the surface thereof composed of a ferrous base comprising immersing the bearing, without prior fluoride activation of the surface thereof, in the above immersion coating bath solution.

Description

A TIN COATING IMMERSION SOLUTION AND A COATING PROCESS USING THE SAME

The present invention relates to the tin plating of bimetal bearings containing aluminum alloys. More particularly, the present invention relates to an immersion coating bath solution for depositing a tin coating on a composite bearing structure which has one surface composed of an aluminum base metal (i.e., aluminum or an alloy of aluminum) and another surface composed of a ferrous base metal (i.e., iron or an alloy of iron) and to an improved process for depositing a tin coating on such bearings utilizing said immersion bath solution.

As described in U.S. Patent 4,170,525 the deposition of a thin coating or plating of tin on the surface of bearings composed of aluminum or aluminum alloys in order to impart a pleasing appearance thereto or to provide corrosion protection therefor, or to provide a "run-in" surface is well known in the art.

Specifically, it is common practice to apply a thin coating of tin to the surface of a bearing by means of electrodeposition to achieve such results. While this technique has met with success, there are certain inherent disadvantages associated therewith. For example, an external electrical power source must be provided and the parts must be properly oriented in the plating bath in order to obtain a satisfactory deposit thereon. In addition, an electrodeposition technique also suffers from the fact that it is difficult to apply thin layers of metal to a structure having a complicated surface configuration. Accordingly, while this technique can find use as a means of applying a thin layer of tin to the surface of a bearing structure it suffers from certain inherent limitations due to the above-mentioned difficulty.

Another well known technique for coating the surface of a bearing with tin is the so-called immersion plating process. In this process, metal is deposited from its salt on the surface of the bearing without the aid of an outside source of electrical current or of chemical reducing agents. This process is especially appealing in that thin coatings of uniform thickness can be readily applied to a structure having a complicated surface configuration. Immersion tin plating baths are either alkaline or acidic. While both types of baths can be used to deposit tin on the surface of aluminum or aluminum alloy, none of the heretofore known baths can be used to satisfactorily apply a thin tin coating to a composite structure having one surface composed of an aluminum base metal and other surface composed of a ferrous base metal. Specifically, alkaline tin immersion baths do not coat both the aluminum and ferrous base metals, but only the aluminum base metal. In addition, the adhesion of tin to the aluminum base metal is generally poor and tends to blister and peel. Various immersion acid tin plating baths have been used quite successfully to deposit a thin layer of tin on a structure which is all aluminum or an alloy thereof, however, when such plating baths are employed to apply a thin layer of tin to a composite structure having a surface composed

of an aluminum base metal and another surface composed of a ferrous base metal, the tin deposit so obtained does not exhibit good adhesion to both metal surfaces. To overcome this problem, it is known in the art to apply tin to the surface of the aluminum base metal by immersion plating techniques and to apply tin to the ferrous base metal surface by electrodeposition. Obviously, this procedure is quite involved and is to be avoided, if possible.

Another well known technique for depositing a thin layer of tin on a surface is the so-called contact plating technique. In this technique, the article to be tinned is usually in direct contact with a piece of tin or zinc in the solution. The contact process is in effect an electrolytic method, with the outside source of currents being replaced by a galvanic couple. However, when conventional contact plating baths are utilized to apply tin to a composite structure having a ferrous base metal surface and an aluminum base metal surface, the coating obtained on the aluminum base metal surface is generally of a very poor quality. This is due to the fact that conventional contact plating baths are designed to produce the desired coating on only the more noble metals.

In U.S. Patent 4,170,525 there is described and claimed a method of concurrently coating the surface of a composite bearing structure having one portion of the surface area thereof composed of an aluminum base metal and another portion of the surface area thereof composed of a ferrous base metal with an adherent layer of tin base metal, comprising:

contacting said composite structure with a mineral acid containing ions selected from the group consisting of fluoride ions, fluoride containing ions or mixture thereof to activate the surface of said aluminum base metal; and immersing said composite structure in an aqueous plating bath containing a mineral acid, a source of ions selected from the group consisting of fluoride ions, fluoride containing ions or mixtures thereof and a source of stannous ions with said stannous ions being present in an amount ranging from about 1 to about 75 grams per liter, for a period of time sufficient to cause tin to be deposited concurrently on said aluminum base metal surface by the exchange of aluminum ions for tin ions and on said ferrous base metal surface by means of a galvanic couple formed between said aluminum base metal and said ferrous base metal.

As will be noted, said patent specifically requires a pretreatment step of fluoride activation of the surface of said aluminum base metal before immersing said composite structure in an aqueous plating bath containing stannous ions which pretreatment step obviously increases the cost complexity of the plating process.

According to the present invention, there is now

provided an immersion bath solution for depositing a tin coating on such bearings without the need for prior fluoride activation of the surface of said aluminum base metal and using less components than previously suggested by the prior art.

The present invention also provides a process for depositing a tin coating on such a bimetal bearing without prior fluoride activation of the surface thereof, and therefore constitutes a major commercial advancement over the process described and claimed in U.S. Patent 4,170,525.

Thus, in accordance with the present invention, there is now provided an immersion coating bath solution for the pretreatment of a bimetal bearing having one portion thereof composed of an aluminum base metal and another portion of the surface thereof composed of a ferrous base metal, said solution having an acidic pH and comprising a water soluble stannous salt and a wetting agent.

The wetting agent used in the immersion coating bath solutions of the present invention are preferably non-ionic such as those formed as the reaction product of ethylene oxide and nonylphenol and sold under the trademark Tergitol NP-9 and Tergitol NP-10 as nonylphenol polyethylene glycol ethers. However, other non-ionic surfactants which are compatible with the immersion coating bath solution may also be utilized. Such wetting agents which include e.g., octyl- phenoxy polyethoxy ethanol non-ionic wetting agents sold under the trademarks Triton X-15, Triton X-100 and Triton X-115 are well known in the art and therefore, will not be discussed herein in detail. The concentration of the wetting agent in the solution is up to about 100 g/l and is preferably about 1-10 g/l.

Said solution also preferably comprises an acid, such as sulfuric or sulfamic acid, to bring the pH of the solution within a range of about 6 to about -0.2 and a solution having a pH range of about 4 to about 0.5 is especially preferred.

While in U.S. Patent 4,170,525 it is stated that the immersion coating bath solution contains a source of ions selected from the group consisting of fluoride ions, fluoride containing ions or mixtures thereof, in fact in all of the preferred examples in said patent, the source of fluoride ions is always fluoboric acid. It has now been found that much superior results are obtained when the immersion coating bath solution further contains a source of fluoride ions other than fluoboric acid, such as ammonium bifluoride, potassium bifluoride, sodium fluoride, sodium silicon fluoride and nickel fluoride.

Furthermore, while said Patent teaches the use of about 3-90 g/l fluoboric acid in the immersion coating bath solution, it has been found according to the present invention that even as little as 1-3 g/l of fluoride ions in the immersion coating bath solution is sufficient to achieve the desired effect and this is even without the prior fluoride activation of the bearing.

In U.S., Patent 4,192,722, there is described and claimed an aqueous alkaline stannate solution, suitable for both immersion and electrolytic plating of aluminum alloys with tin, particularly as an activation step prior to subsequently plating said

alloys with other metals such as bronze, which for activating the 7029 and 7129 aluminum alloys provides an allowable transfer time between the activation bath and subsequent strike bath of at least 45 seconds, said solution comprising:

a) stannate values selected from the group consisting of sodium stannate, potassium stannate, and mixtures thereof;

b) polyhydroxyl carboxylic acid anion values;

c) a hydroxyl compound selected from the group consisting of sodium hydroxide, potassium hydroxide, and mixtures thereof, at free equivalent KOH levels of about 25 grams per liter of said solution.

Said Patent further discloses and claims the inclusion of a chelating agent such as trisodium hydroxyethyl ethylene diamine.

As will be noted, however, said Patent is limited to an immersion coating bath solution for plating aluminum alloys and does not teach or suggest an immersion coating bath solution suitable for plating a bimetal bearing having one portion thereof composed of an aluminum base metal and another portion of the surface thereof composed of a ferrous base.

Furthermore, said solution is alkaline in nature, thus rendering it unsuitable for use with the bimetal of the present invention and further rendering the stannate ions to a value of Sn^{+4} as opposed to the Sn^{+2} values of the immersion coating bath solutions of the present invention.

The concentration of stannous ions in the present invention is achieved by additions of stannous salts, such as stannous sulphate, stannous acetate or other non-halogen containing stannous salts. The concentrations is not critical, but should be a minimum level to initiate the coating. The preferred concentration is between 10 g/L and 60 g/L of stannous ions.

An additional preferred component of the solutions of the present invention is an organic acid such as an organic acid selected from the group consisting of acetic, propionic, citric, tartaric, mallic, succinic and oxalic acid.

Said organic acid can also be substituted by a hydroxy group such as hydroxyacetic acid and dicarboxylic acids are especially preferred. Said organic acids are preferably added in amounts of up to about 80 g/l.

It has also been found that the presence of a saccharide derivative further improves the properties of the immersion coating bath solution and thus said solution also preferably contains a saccharide derivative such as glucose, mannose, galactose, arabinose, xylose, ribose, apiose, aldopentose, erythrose, threose, glyceraldehyde, rhamnose, fucose or fructose.

Said saccharide derivatives are preferably added in amounts of up to about 100 g/l.

The process and solution of the present invention are effective with all bimetal bearings containing aluminum alloys in which the aluminum content is about 50% and are especially preferred for use with an aluminum alloy selected from the group consisting of aluminum-tin-copper, aluminum-silicon-tin

and aluminum-silicon-magnesium.

The present invention also provides a process for depositing a tin coating on a bimetal bearing having one portion thereof composed of an aluminum base metal and another portion of the surface thereof composed of a ferrous base, comprising immersing said bearing, without prior fluoride activation of the surface thereof, in an immersion coating bath solution having an acidic pH and comprising a water soluble stannous salt, and a wetting agent.

Preferably said immersion is carried out at a temperature of about 20° - 40°C, for a period of about 1-3 minutes.

In order to get a good coating of tin on the bi-metal bearing the parts should be clean from all organic contamination and the surface should be clean and active. The preparation of the surface is a simple process sequence, as follows:-

1) Cleaning in alkaline solution (containing sodium carbonate, sodium metasilicate, some complexes, some detergents) for 1-3 minutes at temperatures up to 90°C, or in acid cleaning solution that contains 60-150 g/l H₂SO₄, 20-60 g/l organic alcohols and polyalcohols, such as glucose, glycerine T.E.A. etc., and a wetting agent for about 1-3 minutes at a temperature of about 40-60°C, and

2) Immersion in the chemical tin solution of the present invention at operating temperature for 1-3 mins.

In order to get a white and adherent coating on the bi-metal bearing the bearing is immersed for the required time to achieve a deposit thickness of 0.1 - 0.6 microns. The final deposit thickness is achieved when all the pores of the coating are substantially filled and the chemical replacement has substantially ceased or the rate thereof is very slow. The time to achieve this thickness depends on the concentration of tin, concentration of other constituents, operating temperature, and is typically less than 3 minutes.

While the invention will now be described in connection with certain preferred embodiments in the following examples so that aspects thereof may be more fully understood and appreciated, it is not intended to limit the invention to these particular embodiments. On the contrary, it is intended to cover all alternatives, modifications and equivalents as may be included within the scope of the invention as defined by the appended claims. Thus, the following examples which include preferred embodiments will serve to illustrate the practice of this invention, it being understood that the particulars shown are by way of example and for purposes of illustrative discussion of preferred embodiments of the present invention only and are presented in the cause of providing what is believed to be the most useful and readily understood description of preferred formulations as well as of the principles and conceptual aspects of the invention.

The following examples set for tin immersion coating bath solutions prepared and tested according to the present invention.

EXAMPLE 1

SnSO₄ 20 g/lit
H₂SO₄ 30 cc/lit
Tergitol NP-10 2 g/lit
pH = 2

EXAMPLE 2

SnSO₄ 20 g/lit
H₂SO₄ 30cc/lit
Tergitol NP-10 2 g/lit
Tartaric acid 40 g/lit
pH = 0-1

EXAMPLE 3

SnSO₄ 30 g/lit
UREA 40 g/lit
EDTA 38 g/lit
Tartaric acid 40 g/lit
NH₄HF₂ 5 g/lit
Glucose 40 g/lit
Tergitol NP-10 0.5 g/lit
pH = 0-1

EXAMPLE 4

SnSO₄ 20 g/lit
UREA 30 g/lit
Citric acid 30 g/lit
Gvadrol 30 g/lit
NH₄HF₂ 8 g/lit
Glucose 30 g/lit
Triton X-100 2.5 g/lit
pH = 1-3

EXAMPLE 5

SnSO₄ 20 g/lit
H₂SO₄ 10 cc/lit
Tartaric Acid 30 g/lit
KH₂F₂ 3 g/lit
Triton X-100 2.5 g/lit
pH = 0-1

EXAMPLE 6

SnSO₄ 25 g/lit
Tartaric Acid 50 g/lit
KHF₂ 2 g/lit
Glucose 40 g/lit
Triton X-100 2 g/lit
CuSO₄ 0.5 g/lit
pH = 1-2

EXAMPLE 7

SnSO₄ 15 g/lit
NiSO₄ 7 g/lit
Citric Acid 20 g/lit
Tartaric acid 20 g/lit
NH₄HF₂ 2 g/lit
NP-10 2 g/lit
Fructose 40 g/lit
Urea 20 g/lit
pH = 1-2

EXAMPLE 8

SnSO₄ 20 g/lit
Citric acid 30 g/lit
Tartaric acid 10 g/lit

KHF₂ 2.5 g/lit
Galactose 30 g/lit
MnSO₄ 1 g/lit
Triton x-100 1.5 g/lit
pH = 1-2

EXAMPLE 9

SnSO₄ 20 g/lit
H₂SO₄ 50 g/lit
Tartaric acid 40 g/lit
Glucose 40 g/lit
KHF₂ 5 g/lit
NP-10 1 cc/lit
Triton x-100 2 cc/lit
CuSO₄ 0.5 g/lit
pH = 0-1

EXAMPLE 10

SnSO₄ 20 g/lit
H₂SO₄ 60 g/lit
NP-10 2 cc/lit
KHF₂ 6 g/lit
pH = 0-1

All of the above solution provided a white, adherent tin coating having a thickness of 0.1 - 0.6 microns on bimetal bearings immersed therein.

The following example describes a tin-plating process according to the present invention:

EXAMPLE 11

An aluminum alloy bearing conforming to SAE standard J460e and containing 78.3% aluminum and 20% tin is first placed in an acid cleaner that contains 60 gr/l H₂SO₄, 40 g/l glucose and 15 g/l triton X-100 for 2 min. at a temperature of 50°C. The part is then rinsed in cold running water for 1 min. The bearing is then placed in the tin immersion coating bath solution of example 9 for 2 min and dried. The resulting bearing has a uniform, adherent coating of about 0.4 microns.

EXAMPLE 12

Repeating the procedure of Example 11 with immersion of a cleaned bimetal bearing in the immersion coating bath solution of example 9 for only 30 seconds nevertheless resulted in a bearing having a uniform adherent, white coating of about 0.1 micron.

EXAMPLE 13

Repeating the procedure of Example 11 with immersion of a cleaned bimetal bearing in the immersion coating bath solution of example 10 for one minute resulted in a bearing having a uniform, adherent white coating of about 0.2 microns.

COMPARATIVE EXAMPLE 14

Repeating the procedure of Example 13 however substituting HBF₄ for KHF₂ in the solution of Example 10 and in sufficient amount to provide the equivalent amount of fluoride ions in solution resulted in a coating which was grey in color and non-adherent.

It will be seen from the foregoing that the immersion coating bath solution may contain minor

amounts of other metal ions, in particular Cu⁺⁺, Ni⁺⁺, Mn⁺⁺ or Co⁺⁺, for example up to about 15 g CU⁺⁺, 30 g Ni⁺⁺, 20 g Mn⁺⁺, 15 g Co⁺⁺, or mixtures thereof

It will be evident to those skilled in the art that the invention is not limited to the details of the foregoing illustrative examples and that the present invention may be embodied in other specific forms without departing from the essential attributes thereof, and it is therefore desired that the present embodiments and examples be considered in all respects as illustrative and not restrictive, reference being made to the appended claims, rather than to the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

20 Claims

1. An immersion coating bath solution for depositing a tin coating on a bimetal bearing having one portion thereof composed of an aluminum base metal and another portion of the surface thereof composed of a ferrous base metal, said solution having an acidic pH and comprising a water soluble stannous salt and a wetting agent.

2. An immersion coating bath solution according to Claim 1, comprising an acid to bring the pH of the solution within a range of about 6 to about -0.2.

3. An immersion coating bath solution according to Claim 1, having a pH of about 4 to about 0.5.

4. An immersion coating bath solution according to any one of Claims 1 to 3 further comprising one or more of the following:

(a) NaHF₂, KHF₂, NH₄, HF₂, KF or NaF or another source of fluoride ions other than fluoroboric acid;

(b) glucose or fructose or another saccharide derivative optionally in an amount of up to 100g/l;

(c) a carboxylic acid optionally substituted by a hydroxy group or another organic acid; or

(d) minor amounts of Cu⁺⁺, Ni⁺⁺, Mn⁺⁺, Co⁺⁺ e.g. up to about 15g Cu⁺⁺ ions, 30g Ni⁺⁺ ions, 20g Mn⁺⁺ ions, 15g Co⁺⁺ ions, or mixtures thereof.

5. An immersion coating bath solution according to Claim 4 wherein said organic acid is acetic, propionic or citric acid, or tartaric, malic, succinic or oxalic acid or another dicarboxylic acid optionally substituted by a hydroxy group.

6. An immersion coating bath solution according to any one of Claims 1 to 5 wherein said wetting agent is a nonylphenyl polyethylene glycol ether or another non-ionic wetting agent, and/or said tin salt is stannous sulphate or stannous acetate, and/or the solution optionally comprises between about 10 and 60 g/l tin ions, and/or said aluminum alloy is aluminum-

tin-copper, aluminum-silicon-tin or aluminum-silicon-magnesium.

7. A process for depositing a tin coating on a bimetal bearing having one portion thereof composed of an aluminum base metal and another portion of the surface thereof composed of a ferrous base metal, comprising immersing said bearing, without prior fluoride activation of the surface thereof, in an immersion coating bath solution comprising a water soluble stannous salt and a wetting agent, said solution having an acid pH.

8. A process according to Claim 7 wherein said immersion is carried out at a temperature of about 20°-40°C and/or said immersion is carried out for a period of about 1-3 minutes.

9. A process according to Claim 7 wherein said bearing is subject to acid cleaning prior to immersion in said solution, said acid cleaning solution optionally comprising 60-150 g/l H₂SO₄, 20-60 g/l glucose and a non-ionic wetting agent and/or the cleaning is performed for about 1 to 3 minutes at a temperature of about 40°-60°C.

10. A process according to Claim 7 wherein the immersion coating bath solution is as defined in any one of Claims 2 to 6.

Claims for the following Contracting States: ES.

1. A process for depositing a tin coating on a bimetal bearing having one portion thereof composed of an aluminum base metal and another portion of the surface thereof composed of a ferrous base metal, comprising immersing said bearing, without prior fluoride activation of the surface thereof, in an immersion coating bath solution comprising a water soluble stannous salt and a wetting agent, said solution having an acid pH.

2. A process according to Claim 1 wherein said immersion is carried out at a temperature of about 20°-40°C and/or said immersion is carried out for a period of about 1-3 minutes.

3. A process according to Claim 1 wherein said bearing is subject to acid cleaning prior to immersion in said solution, said acid cleaning solution optionally comprising 60-150 g/l H₂SO₄, 20-60 g/l glucose and a non-ionic wetting agent and/or the cleaning is performed for about 1 to 3 minutes at a temperature of about 40°-60°C.

4. A process as claimed in any one of Claims 1-3 wherein, said immersion coating bath solution comprises an acid to bring the pH of the solution within a range of about 6 to about -0.2.

5. A process as claimed in any one of Claims 1-3 wherein said immersion coating bath solution has a pH of about 4 to about 0.5.

6. A process as claimed in any one of Claims 1-3 wherein said immersion coating bath solution further comprises one or more of the following:

(a) NaHF₂, KHF₂, NH₄, HF₂, KF or NaF or another source of fluoride ions other than

fluoroboric acid;

(b) glucose or fructose or another saccharide derivative optionally in an amount of up to 100g/l;

(c) a carboxylic acid optionally substituted by a hydroxy group or another organic acid;

(d) minor amounts of Cu⁺⁺, Ni⁺⁺, Mn⁺⁺, Co⁺⁺ e.g. up to about 15g Cu⁺⁺ ions, 30g Ni⁺⁺ ions, 20g Mn⁺⁺ ions, 15g Co⁺⁺ ions, or mixtures thereof.

7. A process as claimed in Claim 6 wherein said organic acid is acetic, propionic or citric acid or tartaric, mallic, succinic or oxalic acid or another dicarboxylic acid optionally substituted by a hydroxy group.

8. A process as claimed any one of Claims 1-7 wherein said wetting agent is nonylphenol polyethylene glycol ether or another non-ionic wetting agent and/or said tin salt is stannous sulphate or stannous acetate, and/or the solution optionally comprises between about 10 and 60 g/l tin ions, and/or said aluminum alloy is aluminum-tin-copper, aluminum-silicon-tin or aluminum-silicon-magnesium.



European Patent
Office

EUROPEAN SEARCH REPORT

Application number

EP 88301123.1

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	GB - A - 2 019 895 (GOULD INC.). * Page 2, lines 90-100; page 3, lines 28-42; claims, especially claim 3*	1-4,7	C 23 C 18/46 C 23 C 18/48 C 23 C 18/54
A	GB - A - 1 436 645 (KOLLMORGAN CORPORATION) * Claims *	1,7	
A	EP - A2 - 0 187 482 (TEXO CORPORATION) * Example 1; claim 1 *	1-3,7	
A	EP - A1 - 0 167 949 (RIEDEL-DE HAEN AKTIENGESELLSCHAFT) * Claims *	1-4,7	TECHNICAL FIELDS SEARCHED (Int. Cl.4) C 23 C
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 13-04-1988	Examiner SLAMA
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			